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**CATIONIC POLYMERIZATION OF
VINYL-SUBSTITUTED MONOMERS WITH
 α , α , α' , α' —TETRAPHENYL-P-XYLYL
BISCARBONIUM HEXACHLOROANTIMONATE**

FREDERICK L. HEDBERG

TECHNICAL REPORT AFML-TR-73-38

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FOREWORD

This report was prepared by the Polymer Branch, Nonmetallic Materials Division. The work was initiated under Project No. 7340, "Nonmetallic and Composite Materials", Task No. 734004, "Synthesis of Novel Polymer Materials for High Temperature Resin Applications". It was administered under the direction of the Air Force Materials Laboratory, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Dr. F. E. Arnold (AFML/MBP) as the Project Scientist.

This report covers work conducted from October 1970 to August 1971.

This report was submitted by the author February 1973.

This technical report has been reviewed and is approved.


R. L. VAN DEUSEN
Chief, Polymer Branch
Nonmetallic Materials Division
Air Force Materials Laboratory

ABSTRACT

The hexachloroantimonate salt of the $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-p-xylyl biscarbonium ion has been investigated as an initiator of cationic polymerization of vinyl compounds. This biscarbonium ion salt was found to be ineffective for initiating polymerization of vinyl aliphatic compounds, but effective for initiating polymerization of vinyl ethers. The mechanism of vinyl ether polymerization with this initiator was studied by end-capping reactions. The initiator was found to be incorporated into the polymer indicating an addition mechanism, but no evidence of end-capping groups was found, indicating the absence of "living" dicationic polymer chains.

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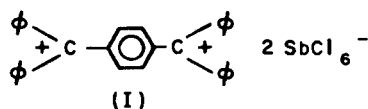
SECTION I

INTRODUCTION

The use of carbonium ion (References 1 and 2) and biscarbonium ion (Reference 3) salts for initiating the polymerization of tetrahydrofuran have been reported. Polymerization of tetrahydrofuran with such initiators has been postulated to proceed by a hydride abstraction mechanism for salts of the triphenylcarbonium ion type (Reference 3) and an electron transfer mechanism for tropylium ion salts (Reference 2). There was no evidence in either case of incorporation of initiator into the polymer as would occur if a simple addition mechanism were operative. The biscarbonium ion thus gave rise to only singly charged polymeric chains rather than the double charged chains reported (Reference 4) for polymerization of tetrahydrofuran by an addition mechanism with a bisoxonium ion salt as initiator.

Besides tetrahydrofuran, carbonium ion salts have also been used to initiate polymerization of vinyl ethers and vinyl aromatics (Reference 5). The mechanism for vinyl ether polymerization with triphenyl carbonium ion salts was postulated as an addition mechanism (Reference 5).

We have investigated the use of the hexachloroantimonate salt of the $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-p-xylyl biscarbonium ion (I) (Reference 6) as an initiator of cationic polymerization. The first objective was to determine whether or not (I) would effect polymerization of vinyl aliphatic compounds, whose polymerization by carbonium ion initiators has not been reported. A second objective was to see if polymerization of vinyl ethers by (I) would occur by an addition mechanism at both ends of (I) to give rise to "living" dicationic polymer chains analogous to those reported (Reference 4) for tetrahydrofuran polymerized by a bisoxonium ion salt.

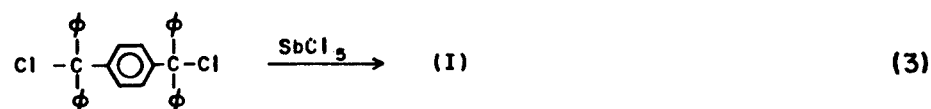
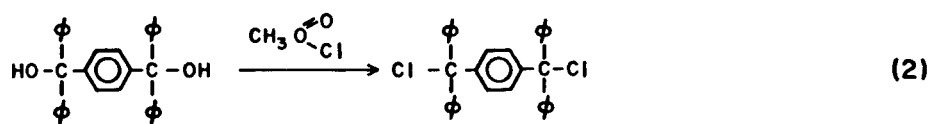
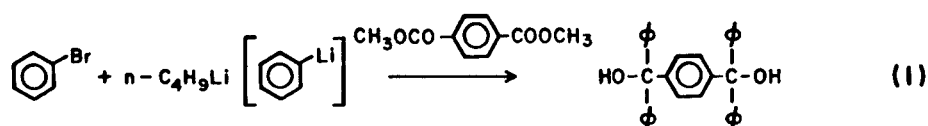


SECTION II

RESULTS AND DISCUSSION

1. SYNTHESIS OF I

The synthesis of (I) was accomplished in three steps, using standard procedures. The first step (Equation 1)



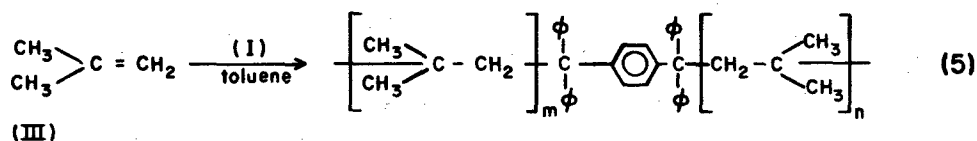
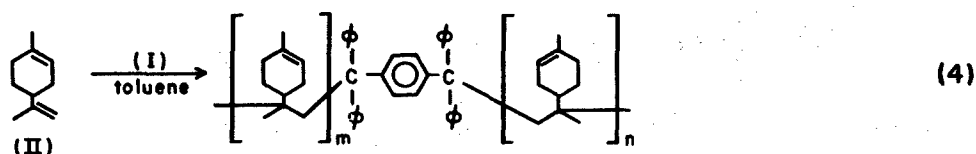
proceeded in good yield (92%) to afford $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-p-xylene- α, α' -diol of sufficient purity that it was used for the second step without further purification. The second step (Equation 2) was carried out in two separate runs, giving crude yields of 67% and 42%. The two batches of crude product were combined for further purification to give 25% of pure $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-p-xylene- α, α' -dichloride. The third step (Equation 3) carried out in toluene afforded (I) as a virtually quantitative yield of dark red precipitate.

(I) is almost completely insoluble in nonpolar solvents such as cyclohexane, toluene, CCl_4 and CH_2Cl_2 . Appreciable solubility was shown by (I) in nitrobenzene, nitromethane, and acetonitrile. The

resistance to hydrolysis of (I) appeared to be quite good, but it was nonetheless always prepared immediately before use. Isolation of dry (I) was carried out only once to verify the reported (Reference 6) quantitative yield. In the remainder of the polymerization reactions, the damp filter cake of (I) was slurried in toluene and used as such.

2. ATTEMPTED POLYMERIZATION OF VINYL ALIPHATICS WITH (I)

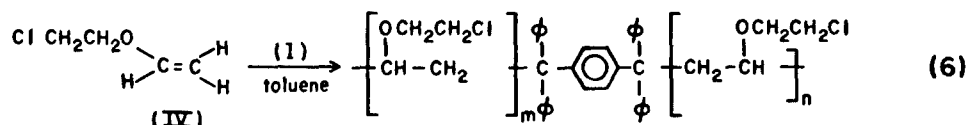
Two vinyl aliphatic compounds, D-limonene (II) and isobutylene (III), were reacted with catalytic amounts of (I) under various conditions in attempts to synthesize the indicated polymers (Equations 4 and 5).



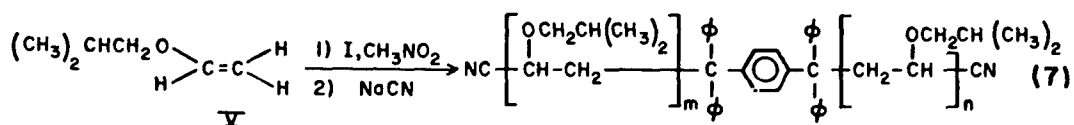
No polymerization occurred in either reaction. For D-limonene, the reaction temperatures used varied from -78°C to that of boiling toluene. At the lower temperatures a heterogeneous system was present, while at the higher temperatures the catalyst was gradually destroyed to give a homogeneous system. With isobutylene the reaction was also carried out in the more polar solvent, nitrobenzene, in which (I) is appreciably soluble. The lack of reaction in all instances indicates that the stability of the carbonium ion sites in (I) is apparently much too great relative to that of a tertiary aliphatic carbonium ion for the initiation step to occur.

3. POLYMERIZATION OF VINYL ETHERS WITH (I)

The homopolymerization of 2-chloroethyl vinyl ether (IV) has not been reported in detail, as this monomer has usually been used for copolymer formation with other vinyl monomers. As the most abundant vinyl ether on hand, however, it was used to test the scope and mechanism of (I) as an initiator. Polymerization of (IV) with (I) was carried out between -78°C and 23°C according to Equation 6.



Low molecular weight polymers were obtained ($\text{Ninh} = 0.13$ and 0.038 for separate runs) indicating that a chain terminating reaction was probably operative. The polymerization was then carried out in nitromethane both to learn the effect of a polar solvent and homogeneous reaction medium, and to afford solubility for the sodium cyanide which was used in an attempt to end-cap the polymer. A low yield of polymer was obtained which was considerably less viscous than that obtained from the reactions in toluene. Infrared analysis indicated that no nitrile groups were present in the polymer, thus ruling out the presence of "living" dicationic polymer chains. An analogous attempt was made to polymerize isobutyl vinyl ether (V) with (I) and end-cap the resultant polymer chain with sodium cyanide as shown in Equation 7.



Again, no nitrile groups were detected by infrared analysis, and only a low molecular weight oil was produced.

The ultraviolet spectrum of the polymer from (V) revealed an intense absorption maximum at about 240 m μ with a shoulder at 260 m μ . Since the polyvinyl ether itself would not be expected to show any significant absorption above 200 m μ , the absorption shown can be attributed to the inclusion of phenyl groups in the polymer. This result supports the assumption of an addition mechanism for the initiation step in the polymerization.

4. CONCLUSIONS

While a biscarbonium ion salt such as (I) would be expected to be somewhat more reactive than the corresponding triphenylcarbonium ion salt, it is apparent from these results that the reactivity of (I) is still far below that necessary to effect polymerization of vinyl aliphatic compounds. Polymerization of vinyl ethers does occur with (I) as initiator, with an initiation mechanism involving addition of (I) to the monomer. This study has not determined if such an initiation process occurs at both ends of (I). The negative results obtained from the end-capping experiments indicate, however, that whether monocationic or dicationic chains are involved in the propagation a "living" polymer is not produced. Chain termination reactions are thus just as prevalent with (I) as initiator as with other common initiators of vinyl ether polymerization.

SECTION III

EXPERIMENTAL

1. $\alpha, \alpha, \alpha', \alpha'$ -TETRAPHENYL-P-XYLENE- α, α' -DIOL

A solution of bromobenzene (94.2 g, 0.60 mole) in anhydrous ether (1300 ml) was stirred at -78°C under nitrogen while a solution of n-butyllithium in hexane (275 ml, 0.55 mole) was added over a 15 minute period. The cooling bath was removed and the reaction mixture was allowed to warm to 0°C over a 70 minute period. The phenyllithium solution was maintained at 0°C with an ice bath while dimethyl terephthalate (19.4 g, 0.100 mole) was added over a 15 minute period in small portions. During the addition, the color changed from a pale bluish gray to a deep orange. The cooling bath was removed and the reaction mixture was allowed to stir at 23°C for 19 hours. During this time, the color changed to deep yellow and a large amount of yellow precipitate formed. Distilled water was added, with stirring, causing at first a clear, pale yellow ether layer above the clear, colorless, water layer. After a few minutes of stirring, a voluminous white precipitate formed. The whole reaction mixture was passed through a coarse porosity sintered glass funnel and the precipitate was slurried in petroleum ether and refiltered to give 32.1 g of $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-p-xylene- α, α' -diol, m.p. $166-168^{\circ}\text{C}$ (lit. 169°C (Reference 7)). The ether layer from the filtrate was separated and boiled down to ca. 200 ml. Cooling afforded separation of 8.1 g more of white product, m.p. $164-166^{\circ}\text{C}$ after filtration and washing with petroleum ether. Dilution of the ether filtrate with petroleum ether to 1 liter gave an additional 0.5 g for a total yield of 40.7 g (92%).

2. $\alpha, \alpha, \alpha', \alpha'$ -TETRAPHENYL-P-XYLENE- α, α' -DICHLORIDE

$\alpha, \alpha, \alpha', \alpha'$ -Tetraphenyl-p-xylene- α, α' -diol from the previous preparation (22.1 g 0.0500 mole) was stirred and refluxed for 1 hour in xylene (1 liter) during which time ca. 2 ml. of H_2O was collected in a

Dean-Stark trap. The solution was allowed to cool to 100°C and then acetyl chloride (39 g, 0.50 mole) was added. The reaction mixture was refluxed for 1 hour, during which time a yellow coloration occurred, and then stirred at 23°C for 15 hours. A white precipitate formed during this period and was filtered and washed with petroleum ether to give 13.7 g of $\alpha, \alpha, \alpha', \alpha'$ -tetraphenyl-p-xylene- α, α' -dichloride, mp 239-242° (lit. 247°C). The filtrate was concentrated to ca 100 ml and diluted to 1 liter with petroleum ether to give an additional 2.4 g, mp 225-230°C. The yield of crude product was thus 16.1 g (67%).

A second run was made with 18.6 g (0.0421 mole) of diol under the same conditions as above, except that after the 1 hour reflux period 600 ml of distillate was boiled off the reaction mixture. 5.5 g of product was obtained upon cooling the reaction mixture and an additional 3.0 g was obtained after dilution with petroleum ether for a total crude yield of 8.5 g (42%) of m.p. 225-230°C.

The combined crudes from both reactions were recrystallized from benzenecyclohexane to give 11.1 g (27%) of purified product, m.p. 246-248°C.

3. $\alpha, \alpha, \alpha', \alpha'$ -TETRAPHENYL-P-XYLYL BISCARBONIUM
HEXACHLOROANTIMONATE (I) (TYPICAL PROCEDURE)

$\alpha, \alpha, \alpha', \alpha'$ -Tetraphenyl-p-xylene- α, α' -dichloride (0.080 g, 0.00017 mole) was dissolved by warming in dry toluene (75 ml). The solution was cooled to 23°C and then ca. 2 g of antimony pentachloride was added. The red suspension which formed was swirled for 1 minute and then filtered and washed by slurring first with toluene and then with cyclohexane. The product was then filtered and sucked dry to give 0.176 g (98%) of dark orange, microcrystalline material.

4. ATTEMPTED POLYMERIZATION OF D-LIMONENE (II)

A solution of freshly distilled D-limonene (10 g, 0.073 mole) in dry toluene (250 ml) was stirred at -78°C under nitrogen while a

suspension of (I) (from 0.1 g, 0.00021 mole of dichloride) in toluene (25 ml.) was added. The resultant red suspension was allowed to warm, with stirring, to 23°C, during which time a yellow solution formed. Removal of solvent left a residue of limonene. Further evaporation of limonene left only a trace of oily solid which was not further characterized.

The reaction was repeated with the same amounts of reactants and catalyst, except that the temperature was maintained at 23°C during addition and the subsequent 1 hour reaction period. No temperature rise was noted upon addition of (I) and after 15-20 minutes of stirring, the red suspension again faded to a pale yellow solution. Evaporation of the reaction mixture to dryness again left only a trace of solid material.

In a third attempt at polymerization, D-limonene (25 g, 0.18 mole) and (I) (from 0.202 g, 0.000042 mole of dichloride) were stirred and refluxed in dry toluene (200 ml) for 2 hours. Concentration to 30 ml and dilution with 500 ml of methanol gave no precipitate and evaporation of solvent left only a small amount of oily brown solid.

5. ATTEMPTED POLYMERIZATION OF ISOBUTYLENE (III)

Suspension method

A solution of isobutylene (50 g, 0.89 mole) in dry toluene (200 ml) was stirred at -78°C under nitrogen while a suspension of (I) from 0.160 g, 0.00033 mole of dichloride) in toluene (75 ml.) was added. The reaction mixture was stirred for 15 minutes at -78°C and then allowed to warm to 23°C over a 1 hour period. A red suspension was still present. Addition of ethanol (700 ml.) afforded a clear yellow solution. Evaporation of the reaction mixture left only a small amount of solid material which was not further characterized.

Solution method

A stirred mixture of nitrobenzene (100 ml) and toluene (100 ml) was refluxed for 1 hour while the trace of water present was collected in a Dean-Stark trap. The mixture was then cooled to -40°C under nitrogen.

Isobutylene (42 g, 0.75 mole) was added, and then a solution of (I) (from 0.080 g, 0.0016 mole of dichloride) in nitrobenzene (25 ml) was added. No temperature change was noted. The reaction mixture was stirred at -40°C for 15 minutes (some crystallization of the nitrobenzene occurred) and then was allowed to warm to 20°C over a 1 hour period, affording a red solution. Addition of 500 ml of ethanol gave a clear yellow solution, the red color fading with addition of the first few drops of ethanol. Evaporation of solvent again left only a small amount of solid material which was not further characterized.

6. POLYMERIZATION OF 2-CHLOROETHYL VINYL ETHER (IV)

A solution of freshly distilled 2-chloroethyl vinyl ether (13.7 g, 0.13 mole) in dry toluene (100 ml) was stirred at -78°C under nitrogen while a suspension of (I) (from 0.10 g, 0.000021 mole of dichloride) in dry toluene (25 ml) was added. After 15 minutes at -78°C the cooling bath was removed and the red suspension was allowed to warm to 23°C over a 1 hour period during which time an almost colorless solution formed. The reaction mixture was stirred an additional hour at 23°C and then diluted with ethanol (600 ml). A large amount of oily white precipitate separated. This was allowed to settle and the supernatant liquid was decanted. The residue was reprecipitated successively from benzene-ethanol twice, acetonitrile-ethanol, and methylene chloride-cyclohexane. An attempt to dissolve the material by heating in cyclohexane was unsuccessful, causing some yellowing of the precipitate which stuck to the bottom of the flask during the heating operation. A subsequent reprecipitation from methylene chloride-cyclohexane still gave yellow colored material. After drying for 48 hours at 23°C in a vacuum oven, 11.4 g (84%) of poly-2-chloroethyl vinyl ether was obtained. The η_{inh} measured in chloroform was 0.13. It was very sticky and gum-like and darkened upon standing for a few weeks.

A second run was carried out under the same conditions as described above, except that only two reprecipitations of the product were made (from benzene with ethanol). The η_{inh} of the gummy product, measured in

chloroform, was 0.038. The yield was 48%, but some of the product was lost during the drying process by foaming in the vacuum oven.

7. ATTEMPTED ENDCAPPING OF POLY (2-CHLOROETHYL VINYL ETHER).

A solution of 2-chloroethyl vinyl ether (25 g, 0.24 mole) in dry nitromethane (200 ml) was stirred at 0°C under nitrogen while a suspension of (I) (from 0.182 g, 0.00038 mole of dichloride) in dry toluene (25 ml) was added. An orange solution resulted which gradually faded to colorless during 45 minutes of stirring at 0°C. After this period, sodium cyanide (0.49 g, 0.010 mole) was added, and stirring was continued at 23°C for 3 hours. The reaction mixture was then diluted with 700 ml of ethanol, forming a cloudy emulsion from which only a small amount of oil settled. The supernatant liquid was decanted and the residue was reprecipitated twice from acetone with ethanol. After drying in a vacuum oven at 23°C, an 11% yield was obtained. An infrared spectrum of the material was virtually identical with that of the poly (2-chloroethyl vinyl ether) from the previous preparation. No nitrile absorption was present. An ultraviolet spectrum was run in dimethoxyethane from 200-350 mμ. An intense maximum was present at 240 mμ with a shoulder at 260 mμ, indicative of phenyl absorption.

8. POLYMERIZATION OF ISOBUTYL VINYL ETHER WITH ATTEMPTED END-CAPPING

A suspension of (I) (from 0.238 g, 0.00050 mole of dichloride) in dry toluene (25 ml) was added to dry nitromethane (150 ml) at 23°C, forming an orange solution. The solution was cooled to 0°C with stirring under nitrogen, and isobutyl vinyl ether (17.2 g, 0.172 mole) was added. The reaction mixture was stirred at 0°C for 1.5 hours. Within 5 minutes, a dark brown coloration occurred which was still present after 1.5 hours. Sodium cyanide (0.49 g, 0.010 mole) was added and stirring at 23°C was continued for 3 hours, during which time the color of the reaction mixture faded to yellow. Cessation of stirring revealed a two-phase liquid system with the lower phase ca. 8 to 10 times greater in volume than the upper phase. Dilution with ethanol (700 ml) afforded a clear yellow one-phase solution. The ethanolic solution was evaporated

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to ca. 200 ml, diluted with CHCl_3 (400 ml) and washed 6 x 1200 ml with water. The yellow CHCl_3 layer was separated and the solvent was evaporated to leave 17 g (100%) of a viscous orange oil. An infrared spectrum showed no nitrile absorption.

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